J. King Saud Univ., Vol. 10, *Science* (2), pp. 119-125 (A.H. 1418/1998)

CHEMISTRY

Furfural from Some Edible Plants Grown in Saudi Arabia

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(Received 27 September, 1997; accepted for publication 17 February 1998)

Abstract. Some edible plants such as *Petroselinum horpense, Eruca sativa, Corchorus olitorius, Lactuca sativa, Cucumis sativus, Spinacia oleracea, Portulaca oleracea* widely grown in Saudi Arabia have been tentatively analyzed and estimated for furfural content by colorometric spectrophotometry after hydrolysis in 13% HCl and extracting through xylene-partition method. The study revealed that there is significant variation in furfural percentage amongst the 7 species, which were found to contain furfural in the range 1.60-6.82% (Table 1). The results indicate the potentiality of these plants, which can be considered to be as good sources of pentosans and furfural contents as other widely used sources of agricultural biomass (Table 2).

Introduction

Shortage of raw materials is an important factor limiting industrial growth in a country. Proper utilization of indigenously available organic resources could open up an inexhaustible reservoir of natural resources to meet the various challenges facing developing countries. The finite world reserves of petroleum have generated great interest in the development of hydrolytic processes for the production of fuels and chemical feedstock from biomass [1-3]. Many forms of lignocellulosic biomass containing hemicellulose can be hydrolyzed easily using mineral acid to produce xylose and arabinose, which yield furfural on further decomposition [4]. Furfural is a chemical of considerable importance in a variety of rapidly developing new industries. It is used as a chemical intermediate in herbicides, as a solvent in the refining of lubricating oil and in synthesis of pharmaceuticals. It is also used for many petroleum, nylon, vegetable oil, plastic and synthetic rubber products, and is an important ingredient in the production of resins and brake linings [5].

The government of Saudi Arabia has been putting a great emphasis in developing the agricultural sector as an important strategic planning parameter in the policy of the country. An increase in the total crop area has been achieved from 3.85 million doniums in 1977 to 9.85 million doniums in 1991 [6]. Several kinds of agricultural products of traditional nature as seasonal crops are produced in large quantities to meet the local demand.

The objective of the present work was to study the content of furfural in some edible plants grown in Saudi Arabia such as *Petroselinum horpense, Eruca sativa, Corchorus olitorius, Lactuca sativa, Cucumis sativus, Spinacia oleracea, Portulaca oleracea* using xylene-partition in conjunction with hydrochloric acid hydrolysis [7]. The extracted furfural was determined colorometrically by UV/Visible spectrophotometry [8].

Materials and Methods

Apparatus and reagents

1. Spectrophotometer: Model LKB 4030 UV/Visible (Biochem Cambridge, England) with 10 mm quartz cells.
2. Xylene: Analar Grade
3. Hydrochloric Acid: 13% diluted HCl from 36% concentration.
4. Water: Double distilled water was used throughout.
5. Aniline Acetate: Dissolved 1 ml AR grade aniline in 50 ml glacial acetic acid and 50 ml of EtOH. The reagent develops a slight yellow colour after 2-3 days and must then be discarded.
6. Furfural standard solution: Furfural standard solutions of 2,4,6,8,10,12 and 14 μg/ml were prepared using xylene as an internal solvent.

Different plants namely, *Petroselinum horpense, Eruca sativa, Corchorus olitorius, Lactuca sativa, Cucumis sativus, Spinacia oleracea, Portulaca oleracea* grown in Saudi Arabia were collected from the vegetable markets at Riyadh, Saudi Arabia. The vegetables of the species were first thoroughly washed with cold distilled water to remove any impurities then dried under sunlight. They were then cut to small sizes.

The determination of furfural content was carried out spectrophotometrically using UV/Visible spectrometer Pharmacia Model LKB 4030 by measuring the intensity of red-colour (absorbance) at 540 nm using aniline acetate reagent [8,9].

Standard solution

The reagent grade furfural which was dark brown in colour due to autoxidation was first distilled to yield a clear slight greenish yellow liquid. Then furfural solutions of concentration 2,4,6,8,10,12 and 14 μg/ml were separately prepared in 100 ml volumetric flasks using xylene as solvent.

Sample preparation

A similar method for the preparation of sample was used as described in the previous work [7, 10], with some modifications. In brief, 2.5g of each sample was individually placed in a 100 ml round-bottomed flask. To this 25 ml of 13% HCl and 100 ml of xylene were added and the flask was equipped with a reflux condenser and guard tube. The whole material was refluxed using a heating-mantle for about 3hrs. After cooling to room-temperature, the mixture was poured into a separating funnel. The xylene layer then was separated and collected in a 500 ml conical flask. The aqueous layer was further washed with two fresh 50 ml volumes of xylene and then discarded. The xylene layers were combined in the conical flask and dried over anhydrous sodium acetate overnight.

After filtration to remove the drying agent the clear xylene solution was collected in a defined volumetric flask. The aliquot of the sample of furfural extracted was diluted with xylene in the defined volumetric flask and made up to the mark using fresh xylene solvent.

Colorimetric analysis

The determination of furfural concentration of the 7 edible plants samples was carried out spectrophotometrically by measuring the intensity of red-colour (absorbance) at 540 nm using aniline-acetate-xylene method [8,9].

To a 5 ml sample-xylene solution in a colorimetric tube, 5 ml of freshly prepared aniline-acetate reagent was added. The mixture was allowed to stand for 20 ± 02 minutes at room-temperature in darkness to develop the red-colour. Then the absorbance of the red-colour was measured at 540 nm using the UV/Visible spectrophotometer along with the standard furfural solutions.

Results and Discussion

The raw materials contained hemicellulose could be hydrolyzed easily using minerals acids, to produce xylose and arabinose, which yield furfural on further hydrolysis [9-12].

The furfural analysis of some edible plants grown in Saudi Arabia is given in Table 1. An earlier study by the author on furfural production from date palm (*Phoenix dactylifera L.*) as well as from some agricultural residues showed that they are rich in pentosan content [12,13]. Since the pentosan content has a direct bearing on the furfural percent, it was felt imperative to study further other indigenously available vegetables e.g., *Petroselinum horpense, Eruca sativa, Corchorus olitorius, Lactuca sativa, Cucumis sativus, Spinacia oleracea, Portulaca oleracea,* for furfural concentration and the findings are incorporated in Table 1.

The results of the spectrophotometric determination of furfural percentage in the 7 species of vegetable plants in Table 1 are based on the ratio of furfural weight produced to the original solid dry weight (g/g) of the vegetables.

The isolated furfural was characterized by the colour reaction with aniline acetate solution which is considered as a method of choice, because of the reproducibility of colorant formation from furfural and aniline acetate of s% = ± 1.4 (sugar) which could be considered as being very good [7,9]. The method was found to be very accurate and extremely reproducible [8]. In this method, there is a good solubility of furfural in xylene: the decomposition mixture of sample substance and HCl is topped with a layer of xylene and the direct measurement of concentration of furfural was carried out in xylene at the end of reaction time, where the risk of difficult-to-volatize reaction products of polysaccharides to penetrate into xylene and to cause colorant formation is greater in this method [9]. However, it was observed that the colour intensity decreases with time; so essentially the time interval of 20 ± 2 minutes was kept constant for measuring the concentration of furfural in all samples [9]. The separated acid layer was tested using aniline acetate solution to check for any traces of furfural and the result was found negative.

The calibration graph for the standard furfural sample was a plot of absorbance versus concentration and gave a linear relationship (r = 0.992) over the range of 2-14 parts per million of furfural in a final volume of 100 ml. The absorptivity calculated from the slope of the graph was 0.95×10^4 mol^{-1} cm^{-1} at 540 nm. The reproducibility of the method was determined by running five replicates of a standard solution that contained 14 μg/ml of furfural showing a relative standard deviation of 2.21%.

Table 1. The furfural yield from some vegetable plants grown in Saudi Arabia after hydrolysis in 13% HCl concentration

Name of the edible plant	Furfural (g/g based on dry wt. of plants)	Furfural%
Petroselinum horpense	0.0618	6.18
Eruca sativa	0.0320	3.20
Corchorus olitorius	0.0490	4.90
Lactuca sativa	0.0682	6.82
Cucumis sativus	0.0270	2.70
Spinacia oleracea	0.0436	4.36
Portulaca oleracea	0.0160	1.60

It can be observed from the results summarized in Table 1 that the furfural content in the different species of the edible plants studied is variable from 1.60 per cent for *Portulaca oleracea* to 6.82 per cent for *Lactuca sativa* with 6.18 per cent, 4.90 per cent, and 4.36 per cent for *Petroselinum horpense, Corchorus olitorius* and *Spinacia oleracea* respectively and the difference may be rationalized due to the changes in pentosan content as result of soil, regional and seasonal conditions [14].

A comprehensive analysis of the data generated from similar studies in Table 2 from other agricultural plant residues [15, 16] based on the hydrolysis of the basic agricultural raw materials, for the production of furfural such as olive seeds, cotton stem, cottonseeds hulls, rice husks, nut shell, beechwood chips, sun flower husk, coffee bean shells and cocoa husks revealed that the furfural yields from the above mentioned decorative plants could be considered to be as good as those obtained from latter biomass sources for the production of furfural.

Table 2. The percentage of pentosans and furfural obtained in some agricultural residues

Material	Pentosans	Furfural	Reference
Olive seeds	21-23	5-6	15
Cotton stems	24	-	,,
Cottonseeds hulls	20.1	12.80	,,
Rice husks	16.90	9.80	,,
Nut shells	24	7-8	,,
Beech wood chips	19-21	5-6	16
Coffee bean shells	15.80	10.3	,,
Cocoa husks	15.4	9.0	,,
Sun flower husks	23-25	6-7	,,

From the results in Table 1 it can be concluded that the vegetable plants could be considered as good sources of raw material for their pentosan content and yield a good amount of furfural, a chemical of considerable importance in a variety of rapidly developing new industries.

Acknowledgment. The author is grateful to Research Center, College of Science, King Saud University for its financial support and Mr. A.A. BaOsman for technical assistance in the experiments.

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تقدير الفورفورال في بعض النباتات الصالحة للأكل والمزروعة في المملكة العربية السعودية

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(أستلم في ١٤١٨/٥/٢٦هـ؛ وقبل للنشر في ١٤١٨/١٠/٢٠هـ)

ملخص البحث. تم في هذه الدراسة تقدير الفورفوال في بعض النباتات الصالحة للأكل والمزروعة في المملكة العربية السعودية لما تكوّنه هذه النباتات من أهمية في وجبات المواطنين. وتطرقت هذه الدراسة إلى تقدير الفورفورال في البقدونس، الجرجير، الملوخية، الخس، الخيار، السبانخ والرجلة. ودلت النتائج عند تقدير الفورفورال بالطريقة الطيفية اللونية أن هناك اختلافا في محتويات هذه الأصناف السبعة حيث تراوحت نسبة الفورفورال من ١,٦٠ إلى ٦,٨٢٪ (جدول ١). كما تم مقارنة النتائج مع أصناف أخرى معروفة لتوضيح أهمية محتويات هذه الأصناف من الفورفورال (جدول ٢).